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Prediction of the Current Density at an Electrode at Which Multiple Electrode Reactions Occur under Potentiostatic Control

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at 303.15 K (15), the corresponding values are 2.76 for R = n-Bu and 2.51 for R = n-Am. Both $(i\text{-Am})_4NI$ and $(n\text{-Am})_4NI$ are regarded as dissociated in DMSO at 298.15 K (2). For sulfolane, no data are available, but because of the high dielectric constant, high temperature of measurement, and behavior of similar R_4N^+ salts (17), we assume that they are both completely dissociated.

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Prediction of the Current Density at an Electrode at Which Multiple Electrode Reactions Occur under Potentiostatic Control

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It is often desirable to be able to predict the total current density at an electrode when multiple electrochemical reactions occur there under potentiostatic control. It is also sometimes desirable to include the effect of ionic migration within the diffusion layer upon the predicted total (1) and partial current densities (2). A procedure for doing this can be illustrated by considering the rotating disk electrode (RDE) system and the associated potential distribution near the RDE as shown in Fig. 1 and 2. For simplicity, it is assumed that the concentration of species i in the solution (c_i) and the potential of the solution (Φ) depend only on the normal coordinate y as shown in Fig. 1. This assumption is reasonable for well-supported solutions and small radius disks. Also, it is assumed that no potential drop exists between the reference electrode within its own compartment and the tip of the Luggin capillary tube.

The procedure consists of writing the Butler-Volmer equation for any general electrochemical reaction j in a particular way, including the effect of ionic migration in the flux expression for species i, and writing the boundary conditions for the concentration of species i and the potential in the solution in a specific manner.

Butler-Volmer Equation

The Butler-Volmer equation for electrochemical reaction j can be written as follows

$$i_j = i_{oj,o}\left[\exp\left(\frac{\alpha_{aj}\mathbf{F}}{RT}\eta_{sj}\right) - \exp\left(\frac{-\alpha_{cj}\mathbf{F}}{RT}\eta_{sj}\right)\right] \quad [1]$$

where

$$\eta_{sj} = V - \Phi_o - U_{j,o} \quad [2]$$

$$U_{j,o} = U_j^\theta - \frac{RT}{n_j\mathbf{F}}\sum_i s_{ij}\ln\left(\frac{c_{i,o}}{\rho_o}\right) - U^\theta_{RE} + \frac{RT}{n_{RE}\mathbf{F}}\sum_i s_{i,RE}\ln\left(\frac{c_{i,RE}}{\rho_o}\right) \quad [3]$$

$$i_{oj,o} = i_{oj,ref}\prod_i\left(\frac{c_{i,o}}{c_{i,ref}}\right)^{\gamma_{ij}} \quad [4]$$

and

$$i_{oj,ref} = i_{oj,data}\prod_i\left(\frac{c_{i,ref}}{c_{i,data}}\right)^{\gamma_{ij}} \quad [5]$$

As shown in Eq. [1], anodic and cathodic current densities are defined here to be positive and negative, respectively. Also, s_{ij} is positive for an anodic reactant and negative for a cathodic reactant. As shown by Eq. [2], the current density i_j depends upon the difference between the potential of the electrode (V) and the potential in the solution adjacent to the electrode surface (Φ_o) relative to the open-circuit potential for reaction j ($U_{j,o}$) evaluated at the surface concentrations of species i ($c_{i,o}$). The values of the potentials V, Φ, U_j^θ, and U^θ_{RE} are all relative to the standard hydrogen reference electrode potential which is defined to be zero for convenience. Thus, if the reference electrode used in the experiment is a standard hydrogen reference electrode, $U_{j,o}$ is simply the Nernst equation (1) evaluated at $c_{i,o}$. Note that i_j depends on $c_{i,o}$ through both $U_{j,o}$ and the concentration dependence of the exchange current density as given by Eq. [4], which shows that the exchange current density of reaction j evaluated at the surface concentrations ($i_{oj,o}$) can be written in terms of reference concentrations ($c_{i,ref}$). Also note that Eq. [5] can be used to determine a value for $i_{oj,ref}$ assuming values are known for $i_{oj,data}$, $c_{i,data}$, and γ_{ij}. The open-circuit potential $U_{j,o}$

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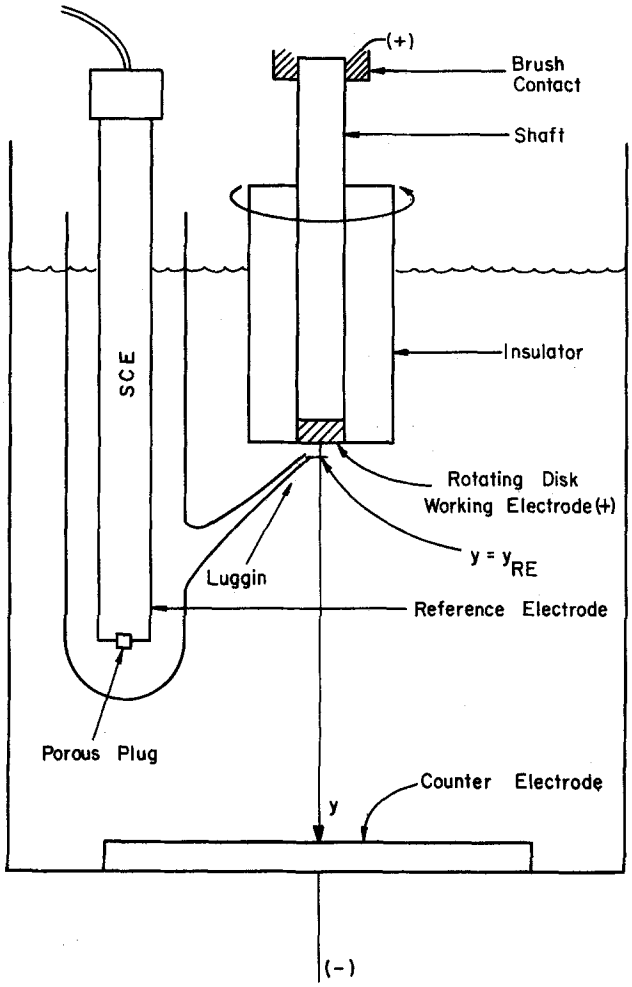

Fig. 1. Schematic of a rotating disk electrode system

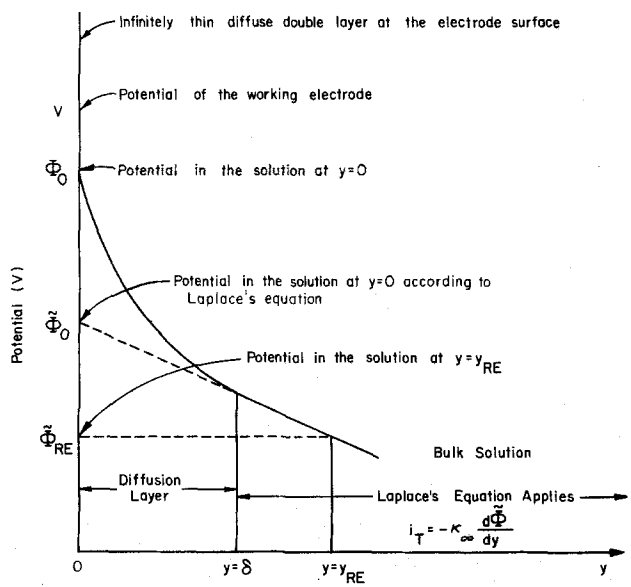

Fig. 2. Schematic of the solution potential profile near an electrode being operated anodically.

can be written in terms of the reference concentrations by adding and subtracting the following term to Eq. [3]

$$\frac{RT}{n_j F}\sum_i s_{ij}\ln\left(\frac{c_{i,ref}}{\rho_o}\right) \qquad [6]$$

The result is

$$U_{j,o} = U_{j,ref} - \frac{RT}{n_j F}\sum_i s_{ij}\ln\left(\frac{c_{i,o}}{c_{i,ref}}\right) \qquad [7]$$

where

$$U_{j,ref} = U_j^\theta - \frac{RT}{n_j F}\sum_i s_{ij}\ln\left(\frac{c_{i,ref}}{\rho_o}\right) - U^\theta_{RE} + \frac{RT}{n_{RE}F}\sum_i s_{i,RE}\ln\left(\frac{c_{i,RE}}{\rho_o}\right) \qquad [8]$$

Also, the potential difference $V - \Phi_o$ in Eq. [2] can be written in terms of the applied or set potential difference $V - \tilde{\Phi}_{RE}$ as follows

$$V - \Phi_o = V - \tilde{\Phi}_{RE} - (\Phi_o - \tilde{\Phi}_{RE}) \qquad [9]$$

where $\tilde{\Phi}_{RE}$ is the potential in the solution at $y = y_{RE}$ (see Fig. 1 and 2).

Now, Eq. [2], [4], [7], and [9] can be used to rewrite Eq. [1] in the desired form

$$i_j = i_{o,jref}\left\{\frac{\pi}{i}\left(\frac{c_{i,o}}{c_{i,ref}}\right)^{p_{ij}}\exp\left(\frac{\alpha_{aj}F}{RT}[V - \tilde{\Phi}_{RE} - (\Phi_o - \tilde{\Phi}_{RE}) - U_{j,ref}]\right) - \frac{\pi}{i}\left(\frac{c_{i,o}}{c_{i,ref}}\right)^{q_{ij}}\exp\left(\frac{-\alpha_{cj}F}{RT}[V - \tilde{\Phi}_{RE} - (\Phi_o - \tilde{\Phi}_{RE}) - U_{j,ref}]\right)\right\} \qquad [10]$$

where

$$p_{ij} = \gamma_{ij} + \frac{\alpha_{aj}s_{ij}}{n_j} \qquad [11]$$

and

$$q_{ij} = \gamma_{ij} - \frac{\alpha_{cj}s_{ij}}{n_j} \qquad [12]$$

It is useful at this point to compare the potential differences in the arguments of the exponentials in Eq. [10]

$$V - \tilde{\Phi}_{RE} - (\Phi_o - \tilde{\Phi}_{RE}) - U_{j,ref} \qquad [13]$$

to those used commonly by others (3) in similar expressions. Typically, the potential differences used by others (3) are

$$E_{appl} - E_{eq} - i_T A R_s \qquad [14]$$

where E_{appl} is defined to be the potential difference between the working electrode and a reference electrode placed in the bulk solution with current being passed in the cell, E_{eq} is that same potential difference when no current is being passed, and $i_T A R_s$ is the ohmic potential drop in the solution between the working and reference electrodes. It should be pointed out that the potential in the solution at y_{RE} depends upon the current being passed; it is not a constant as is often assumed (3). The potential differences given by Eq. [13] and [14] are not the same because, even though

$$E_{appl} = V - \tilde{\Phi}_{RE} \qquad [15]$$

and for a single electrode reaction

$$E_{eq} = U_{j,ref} \qquad [16]$$

the ohmic drop through the diffusion layer is different. That is

$$i_T A R_s \neq \Phi_o - \tilde{\Phi}_{RE} \qquad [17]$$

The ohmic potential drops are not the same because the specific conductivity (κ_∞) of the electrolyte is not constant through the diffusion layer as is often assumed by others (3). That is, if it is assumed that both i_T and κ_∞ are constants through the diffusion layer, then Laplace's equation

$$i_T = -\kappa_a \frac{d\tilde{\Phi}}{dy} \quad [18]$$

can be integrated to give

$$\frac{i_T y_{RE}}{\kappa_a} = \tilde{\Phi}_o - \Phi_{RE} \quad [19]$$

which can be rewritten in terms of the solution resistance (R_s) by using the following equation (3)

$$R_s = \frac{y_{RE}}{\kappa_a A} \quad [20]$$

Thus, by using Eq. [20], Eq. [19] becomes

$$i_T A R_s = \tilde{\Phi}_o - \tilde{\Phi}_{RE} \quad [21]$$

Comparison of Eq. [17] and [21] shows that $\Phi_o \neq \tilde{\Phi}_o$ as illustrated schematically in Fig. 2. Typically, it is assumed, however, that $\Phi_o = \tilde{\Phi}_o$, which is often not true (2, 4).

It should be noted that both E_{appl} and $V - \tilde{\Phi}_{RE}$ depend upon the type of reference electrode used, since they both represent the same physical quantity. (It can be seen that $V - \tilde{\Phi}_{RE}$ must depend upon the type of reference electrode used in the experiment since at equilibrium

$$V - \tilde{\Phi}_{RE} = U_{j,ref} \quad [22]$$

and $U_{j,ref}$ depends upon the type of reference electrode used. (Note that the potential difference $\Phi_o - \tilde{\Phi}_{RE}$ is equal to zero at equilibrium.) In addition, E_{eq} and $U_{j,ref}$ depend in the same manner upon the type of reference electrode used (3). Consequently, the difference between $V - \tilde{\Phi}_{RE}$ and $U_{j,ref}$ is independent of the type of reference electrode used in the experiment, as is $E_{appl} - E_{eq}$.

Governing Equations and Boundary Conditions for c_i and Φ

The governing equation for the concentration of species i at steady-state conditions and no homogeneous reactions is (1)

$$\frac{dN_i}{dy} = 0 \quad [23]$$

where

$$N_i = -D_i \frac{dc_i}{dy} - z_i \frac{D_i c_i F}{RT} \frac{d\Phi}{dy} + v c_i \quad [24]$$

and the governing equation for the potential in the solution is the electroneutrality condition (1)

$$\Sigma z_i c_i = 0 \quad [25]$$

The boundary conditions for a single electrode reaction are as follows

at $y = 0$

$$\Sigma z_i c_i = 0 \quad [26]$$

$$V = \text{a set constant } (e.g., 0.2\text{V}) \quad [27]$$

$$\frac{s_{ij} i_j}{n_j F} = -N_i \quad [28]$$

where N_i is given by Eq. [24] with $v = 0$ and i_j is given by Eq. [10]

at $y = y_{RE}$

$$c_i = c_{i,ref} \quad \text{where} \quad \Sigma_i z_i c_{i,ref} = 0 \quad [29]$$

$$\Phi = \tilde{\Phi}_{RE} = \text{a set constant } (e.g., 0.1\text{V}) \quad [30]$$

It is important to note that both V and $\tilde{\Phi}_{RE}$ must be set such that their difference $(V - \tilde{\Phi}_{RE})$ is equal to the value set by the potentiostat.

Once values have been set for the parameters of the system, the solution of Eq. [23] and [25] subject to Eq. [26]-[30] yields values for $c_i(y)$ and $\Phi(y)$. The values of c_i and Φ at $y = 0$ ($c_{i,o}$ and Φ_o) can then be used together with the kinetic parameters to predict the current density of reaction j according to Eq. [10].

If more than one electrode reaction occurs, Eq. [28] must be changed to

$$\sum_j \frac{s_{ij} i_j}{n_j F} = -N_i \quad [31]$$

where i_j is given by Eq. [10] with the appropriate kinetic parameters. The total predicted current density (i_T) can, then, be obtained by solving the equations and summing the current densities due to the individual reactions as follows

$$i_T = \sum_j i_j \quad [32]$$

It is worth noting that even if the effect of ionic migration is negligible, the procedure presented here is useful because it permits the direct use in the model of the set potential difference between the working electrode and a reference electrode in the bulk solution, and it provides a method of predicting the current densities of the individual reactions when multiple electrode reactions occur.

Finally, it should be mentioned that a less direct method could be used for a single electrode reaction but would be difficult to apply for multiple electrode reactions. The procedure would consist of setting i_j in Eq. [28] and, then, determining Φ_o by solving the transport problem. This value of Φ_o could, then, be used in Eq. [10] to obtain $V - \tilde{\Phi}_{RE}$ which could be compared to the observed value and a new i_j selected, if necessary. Since this would be an iterative procedure, it would be difficult to implement particularly for multiple electrode reactions, especially if the current densities due to the individual reactions were not equal, as is often the case.

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LIST OF SYMBOLS

A	area of the electrode, cm^2
c_i	concentration of species i, mol/cm^3
$c_{i,o}$	local surface concentration of species i, mol/cm^3
$c_{i,data}$	data concentration of species i, mol/cm^3
$c_{i,ref}$	reference concentration of species i, mol/cm^3
D_i	diffusion coefficient of species i, cm^2/sec
E_{appl}	potential of working electrode relative to potential of a reference electrode of a given kind, V
E_{eq}	potential of working electrode relative to potential of a reference electrode of a given kind when no current is passed, V
F	Faraday's constant, 96,487 C/mol
i_j	current density due to reaction j, A/cm^2
$i_{oj,data}$	exchange current density at concentrations reported in the literature ($c_{i,data}$), A/cm^2
$i_{oj,ref}$	exchange current density at reference concentrations, A/cm^2
i_T	total current density, A/cm^2
n_j	number of electrons transferred in reaction j
p_{ij}	anodic reaction order of species i in reaction j
q_{ij}	cathodic reaction order of species i in reaction j
R	universal gas constant, 8.3143 J/mol K
R_s	solution resistance, Ω
s_{ij}	stoichiometric coefficient of species i in reaction j
T	absolute temperature, K
$U_{j,o}$	theoretical open-circuit potential for reaction j

at the surface concentrations of the species i which participate in reaction j, V

$U_{j,ref}$ theoretical open-circuit potential evaluated at reference concentrations, V

U_j^θ standard electrode potential for reaction j, V

V potential of the working electrode, V

y normal coordinate, cm

y_{RE} position of the reference electrode, cm

z_i charge number of species i

Greek Symbols

α_{aj} anodic transfer coefficient for reaction j

α_{cj} cathodic transfer coefficient for reaction j

γ_{ij} exponent in the composition dependence of the exchange current density

δ diffusion layer thickness, cm

ρ_o pure solvent density, kg/cm^3

Φ potential in the solution within the diffusion layer, V

$\tilde{\Phi}$ potential in the bulk solution, V

Φ_o solution potential adjacent to electrode surface, V

$\tilde{\Phi}_o$ potential in the solution at $y = 0$ obtained by integrating Laplace's equation with constant i_T and κ_∞, V

$\tilde{\Phi}_{RE}$ potential in the bulk solution at y_{RE}, V

κ_∞ bulk solution specific conductivity, Ω^{-1} cm^{-1}

Subscripts

o at the electrode surface

RE reference electrode

ref reference conditions

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